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Washington, D.C. 20231

Transmitted herewith for filing is the patent application of:

Keisuke OGURO, Kinji ASAKA, Tatsuhiko OKADA,
Kazuo ONISHI and Shingo SEWAJCS11 U.S. PRO
09/25/98

02/19/99

Entitled: "POLYMERIC ACTUATORS AND PROCESS FOR PRODUCING
THE SAME"

Enclosed are:

- ☒ 6 sheets of drawings
- ☒ An Assignment of the invention to: AGENCY OF INDUSTRIAL
SCIENCE AND TECHNOLOGY, MINISTRY OF INTERNATIONAL TRADE
AND INDUSTRY and JAPAN CHEMICAL INNOVATION INSTITUTE.
- ☒ Declaration and Power of Attorney
- ☒ Preliminary Amendment
- ☒ Claim for Priority with certified copies

CLAIMS AS FILED

<u>No. Filed</u>	<u>No. Extra</u>		<u>Small Entity Rate</u>	<u>Non-Small Entity Rate</u>	<u>Charge</u>
Total Claims <u>7</u>	<u>-20</u>	= <u>0</u>	X \$ 9.00	\$ 18.00	\$ <u>0</u>
Indep. Claims <u>2</u>	<u>- 3</u>	= <u>0</u>	X \$ 39.00	\$ 78.00	\$ <u>0</u>
Multiple Dependent Claim/s			\$130.00	\$260.00	\$ <u>0</u>
Basic Fee +			\$380.00	\$760.00	\$ <u>760</u>
Total of above charges					\$ <u>760</u>

Checks in the amounts of \$ 760.00 and \$ 40.00 are enclosed to cover the filing fee and the assignment recording fee.

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An original and two copies of this sheet are enclosed.

February 19, 1999
Date

By Kent E. Baldauf
Kent E. Baldauf, Reg. No. 25,826
Attorney for Applicants
700 Koppers Building
436 Seventh Avenue
Pittsburgh, PA 15219-1818
Telephone: 412/471-8815
Facsimile: 412/471-4094

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of :

KEISUKE OGURO, :
KINJI ASAKA, : POLYMERIC ACTUATORS
TATSUHIRO OKADA, : AND PROCESS FOR
KAZUO ONISHI : PRODUCING THE SAME
and SHINGO SEWA :

Serial No. Not Yet Assigned :

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February 19, 1999

PRELIMINARY AMENDMENT

Box PATENT APPLICATION
Assistant Commissioner for Patents
Washington D.C. 20231

Sir:

Prior to initial examination, please amend the
above-identified patent application as follows:

IN THE SPECIFICATION:

Page 4, line 13, delete "a" (second occurrence)
and insert therefor --the--.

Page 5, line 4, delete "OBJECT OF THE
INVENTION".

Page 17, line 10, delete "is" and insert
--are--.

Page 30, line 14, after "13" insert --is--.

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Page 32, line 17, delete "EFFECT OF THE INVENTION".

Page 32, line 22, delete "make" and insert
--increase--.

Page 32, line 24, delete "increased".

IN THE CLAIMS:

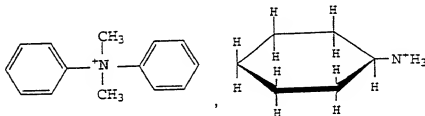
Amend claim 5 and add claims 6 and 7 as follows:

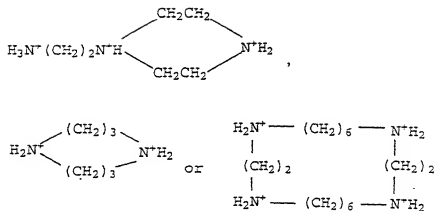
Claim 5, line 1, delete "any one".

Claim 5, line 2, delete "of claims 2 to 4" and
insert therefor --claim 2--.

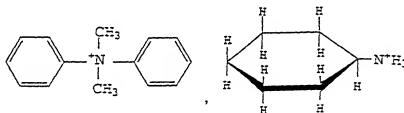
Add claims 6 and 7 as follows:

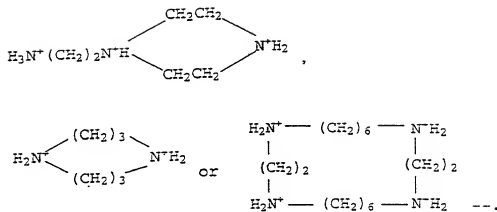
--6. The polymeric actuator as claimed in
claim 3, wherein the ion represented by the
formula (1) is $\text{CH}_3\text{N}^+\text{H}_3$, $\text{C}_2\text{H}_5\text{N}^+\text{H}_3$, $(\text{CH}_3)_2\text{N}^+\text{H}_2$, $(\text{C}_2\text{H}_5)_2\text{N}^+\text{H}_2$,
 $(\text{C}_4\text{H}_9)_2\text{N}^+\text{H}_2$, $(\text{C}_5\text{H}_{11})_2\text{N}^+\text{H}_2$, $(\text{CH}_3)_3\text{N}^+\text{H}$, $(\text{C}_2\text{H}_5)_3\text{N}^+\text{H}$, $(\text{C}_4\text{H}_9)_3\text{N}^+\text{H}$,
 $(\text{C}_5\text{H}_{11})_3\text{N}^+\text{H}$, $(\text{CH}_3)_4\text{N}^+$, $(\text{C}_2\text{H}_5)_4\text{N}^+$, $(\text{C}_3\text{H}_7)_4\text{N}^+$, $(\text{C}_4\text{H}_9)_4\text{N}^+$,
 $\text{H}_3\text{N}^+(\text{CH}_2)_4\text{N}^+\text{H}_3$, $\text{H}_2\text{C}=\text{CHCH}_2\text{N}^+\text{HCH}_3$, $\text{H}_3\text{N}^+(\text{CH}_2)_4\text{N}^+\text{H}_2(\text{CH}_2)_4\text{N}^+\text{H}_3$,
 $\text{HC}\equiv\text{CCH}_2\text{N}^+\text{H}_2$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{N}^+\text{H}_3$, $\text{H}_3\text{N}^+(\text{CH}_2)_5\text{OH}$, $\text{H}_3\text{N}^+\text{CH}(\text{CH}_2\text{OH})_2$,
 $(\text{HOCH}_2)_2\text{C}(\text{CH}_2\text{N}^+\text{H}_3)_2$, $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{N}^+\text{H}_3$,





7. The polymeric actuator as claimed in claim 4, wherein the ion represented by the formula (1) is $\text{CH}_3\text{N}^+\text{H}_3$, $\text{C}_2\text{H}_5\text{N}^+\text{H}_3$, $(\text{CH}_3)_2\text{N}^+\text{H}_2$, $(\text{C}_2\text{H}_5)_2\text{N}^+\text{H}_2$, $(\text{C}_4\text{H}_9)_2\text{N}^+\text{H}_2$, $(\text{C}_5\text{H}_{11})_2\text{N}^+\text{H}_2$, $(\text{CH}_3)_3\text{N}^+\text{H}$, $(\text{C}_2\text{H}_5)_3\text{N}^+\text{H}$, $(\text{C}_4\text{H}_9)_3\text{N}^+\text{H}$, $(\text{C}_5\text{H}_{11})_3\text{N}^+\text{H}$, $(\text{CH}_3)_4\text{N}^+$, $(\text{C}_2\text{H}_5)_4\text{N}^+$, $(\text{C}_3\text{H}_7)_4\text{N}^+$, $(\text{C}_4\text{H}_9)_4\text{N}^+$, $\text{H}_3\text{N}^+(\text{CH}_2)_4\text{N}^+\text{H}_3$, $\text{H}_2\text{C}=\text{CHCH}_2\text{N}^+\text{HCH}_3$, $\text{H}_3\text{N}^+(\text{CH}_2)_4\text{N}^+\text{H}_2(\text{CH}_2)_4\text{N}^+\text{H}_3$, $\text{HC}\equiv\text{CCH}_2\text{N}^+\text{H}_2$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{N}^+\text{H}_3$, $\text{H}_3\text{N}^+(\text{CH}_2)_5\text{OH}$, $\text{H}_3\text{N}^+\text{CH}(\text{CH}_2\text{OH})_2$, $(\text{HOCH}_2)_2\text{C}(\text{CH}_2\text{N}^+\text{H}_3)_2$, $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{N}^+\text{H}_3$,



REMARKS

Amendments have been made to the specification in order to place the specification in conformance with standard United States patent practice.

Claim 5 has been amended to eliminate the multiple dependency and new claims 6 and 7 have been added.

Examination and allowance of pending claims 1-7 are respectfully requested.

Respectfully submitted,

WEBB ZIESENHEIM BRUENING LOGSDON
ORKIN & HANSON, P.C.

By

Kent E. Baldauf
 Kent E. Baldauf, Reg. No. 25,826
 Attorney for Applicants
 700 Koppers Building
 436 Seventh Avenue
 Pittsburgh, PA 15219-1818
 Telephone: 412/471-8815
 Facsimile: 412/471-4094

TITLE

POLYMERIC ACTUATORS AND PROCESS FOR PRODUCING THE SAME

FIELD OF THE INVENTION

5 The present invention relates to novel polymeric actuators and a process for producing the same. More particularly, the invention relates to polymeric actuators functioning as actuators by bending or deforming ion-exchange resin products and to a process
10 for producing the polymeric actuators.

BACKGROUND OF THE INVENTION

 Recently, there is an enhanced demand for a miniaturized, lightweight and highly flexible actuator
15 in the fields of medical equipment, industrial robots, micromachines and the like.

 When the actuator is thus miniaturized, the friction and viscous force are dominant over the inertial force. Therefore, it has been difficult to
20 employ the means for converting energy to motion with the use of inertial force, such as a motor or an engine, as the power source of a microactuator. Accordingly, the operating principles based on electrostatic attraction, piezoelectricity, ultrasonic wave, shape

memory alloy and polymer expansion/contraction have been proposed for the microactuator.

The actuator of the electrostatic attraction type operates by attracting, for example, a plate or rod becoming an electrode toward a counter electrode, and, for example, one which bends an electrode by applying a voltage of about 100 V between the electrode and the counter electrode disposed with a spacing of about tens of microns is known. The piezoelectric actuator operates by applying a voltage of some volts to a piezoelectric element of a ceramic such as barium titanate so that the element is expanded and contracted, and one capable of controlling a nm-unit displacement is known. The ultrasonic actuator operates by combining frictional force with the ultrasonic vibration generated by the piezoelectric element or the like, or by effecting a runoff. The actuator of the shape memory alloy type operates by temperature change with the use of the marked change of the configuration of the shape memory alloy depending on temperature. The actuator of the polymer expansion/contraction type operates with the use of the expansion/contraction of the polymer depending on the temperature or change of pH and change of the concentration of environmental chemical substance.

However, these microactuators have drawbacks in that there is restriction in their respective operation environments, the response is unsatisfactory, the structure is complicated and the flexibility is poor.

- 5 For example, for the operation of the actuator of the polymer expansion/contraction type, the solution in contact with the polymer must be replaced by the solution containing other salt. Therefore, it has been difficult to employ this actuator in the use requiring a
- 10 small size and a rapid response.

- In contrast, an actuator element comprising an ion-exchange membrane and electrodes coupled to surfaces of the ion-exchange membrane and adapted to apply a potential difference to the ion-exchange membrane in the
- 15 hydrous state so that the ion-exchange membrane is curved or deformed has been proposed as one which can be easily miniaturized, realizes rapid response and operates with small electric power (see Japanese Patent Laid-open Publication No. 4(1992)-275078).

- 20 This actuator element is characterized by comprising an ion-exchange resin membrane (ion-exchange resin molding) and metal electrodes coupled to surfaces thereof in mutually insulating relationship and by being adapted to apply a potential difference between the
- 25 metal electrodes while the ion-exchange resin membrane

is in the hydrous state so that the ion-exchange resin membrane is curved or deformed.

- In this actuator element, the electrodes are formed on the surfaces of the ion-exchange resin molding by
- 5 chemical plating, electroplating, vacuum deposition, sputtering, coating, press bonding, fusion bonding or other methods. For example, the conventional process for forming the electrodes by the chemical plating includes a process comprising subjecting the ion-
- 10 exchange membrane to etching of the surfaces thereof, bearing of a plating catalyst and immersion in a plating bath, thereby to form electrodes on the surfaces of the ion-exchange membrane and a process comprising a steps of making the surfaces of the ion-exchange resin
- 15 membrane to adsorb a metal complex, followed by reducing the adsorbed complex, and then immersing the ion-exchange resin membrane in a plating bath to form the electrodes on the surfaces of the ion-exchange membrane.

- However, the actuator element having the electrodes
- 20 formed by the above methods has a drawback in that the displacement level is not satisfactory. In the conventional polymeric actuator, further, when the voltage applied between the electrodes is increased to obtain larger displacement and better response, water in

the ion-exchange resin membrane is easily electrolyzed, and therefore bubbles are easily produced.

OBJECT OF THE INVENTION

- 5 The present invention is intended to solve such problems associated with the prior art as mentioned above, and it is an object of the invention to provide an actuator element capable of generating large displacement, having rapid response and high
- 10 flexibility, having simple structure and capable of being easily miniaturized, and a process for producing the same. It is another object of the present invention to provide a polymeric actuator free from occurrence of bubbles due to electrolysis of water when a potential
- 15 difference is applied.

SUMMARY OF THE INVENTION

- The process for producing a polymeric actuator according to the present invention is a process for
- 20 producing a polymeric actuator comprising an ion-exchange resin product and metal electrodes which are formed on the surface of the ion-exchange resin product and are insulated from each other, said polymeric actuator operating as an actuator by applying a
- 25 potential difference between the metal electrodes when

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the ion-exchange resin product is in the water-containing state to allow the ion-exchange resin product to undergo bending or deformation,

wherein the following steps (i) to (iii) are
5 repeatedly conducted to form the metal electrodes ranging from the surface of the ion-exchange resin product to the inside thereof;

(i) a step of allowing the ion-exchange resin product to adsorb a metal complex in an aqueous solution
10 (adsorption step),

(ii) a step of reducing the metal complex adsorbed on the ion-exchange resin product by a reducing agent to deposit a metal on the surface of the ion-exchange resin product (deposition step), and

15 (iii) a step of washing the ion-exchange resin product having the deposited metal (washing step).

By virtue of the method to form metal electrodes through the above steps, metal deposition further proceeds to the interior of the ion-exchange resin
20 product to increase the contact area between the ion-exchange resin product and the metal electrodes, whereby the number of electrode active spots is increased to thereby increase the quantity of ions which migrate to a negative electrode. In the polymeric actuator, water
25 molecules accompanying the ions migrate to a negative

electrode so that the water content in the vicinity of said electrode is decreased to thereby expand the negative electrode side of the resin product, while the water content in the vicinity of the positive electrode is decreased to thereby contract the positive electrode side of the resin product. Accordingly, when the quantity of ions which migrate to an electrode is increased, the quantity of water molecules which migrate to the electrode together with the ions is also increased. As a result, the difference in the water content between the vicinity of the negative electrode and the vicinity of the positive electrode becomes larger, and the degree of bending (deformation), namely, degree of displacement, is increased. Further, since the thickness of the metal electrode is increased, the surface resistance of the electrode is decreased to raise conductivity of the electrode.

According to the process of the invention, therefore, a polymeric actuator having simple structure, capable of being easily miniaturized, showing quick response and capable of generating large displacement can be obtained.

The polymeric actuator according to the present invention comprises an ion-exchange resin product and metal electrodes which are formed on the surface of the

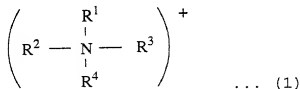
ion-exchange resin product containing an alkylammonium ion as a counter ion and are insulated from each other, said polymeric actuator operating as an actuator by applying a potential difference between the metal

- 5 electrodes when the ion-exchange resin product is in the water-containing state to allow the ion-exchange resin product to undergo bending or deformation.

In the polymeric actuator of the invention, the counter ions of the ion-exchange resin product are

- 10 exchanged with specific alkylammonium ions, and thereby bubbles are hardly produced even under application of a high voltage, differently from the conventional ion-exchange resins whose counter ion is Na^+ or H^+ . In the polymeric actuator, further, water molecules
- 15 accompanying the ions generally migrate to an electrode to increase the water content in the vicinity of said electrode. As a result, this electrode side of the resin product is swollen and expanded, while the water content in the vicinity of the opposite electrode is
- 20 decreased to thereby contract the opposite electrode side of the resin product. Therefore, if the counter ions are exchanged with the alkylammonium ions, the difference in the water content between the electrodes becomes larger, and the degree of bending (deformation),
- 25 namely, degree of displacement, can be increased.

It is preferable that, as the alkylammonium ion, an alkylaluminum ion represented by the following formula (1) is contained. When such ions are contained, the difference in the water content between the electrodes becomes much larger, and the degree of bending (deformation), namely, degree of displacement, can be increased.



10

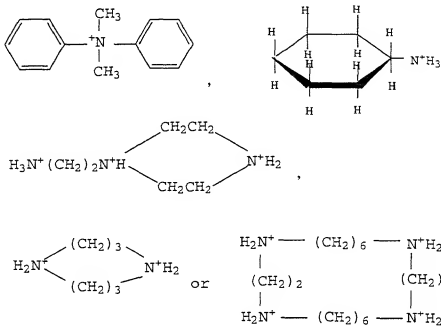
In the above formula, R^1 to R^4 may be the same or different and are each a hydrogen atom, a hydrocarbon group, an oxygen-containing hydrocarbon group or a nitrogen-containing hydrocarbon group, at least one of R^1 to R^4 is a group other than a hydrogen atom, and two or more of R^1 to R^4 may be bonded to form a ring.

In the polymeric actuator of the invention, it is more preferable that the alkylammonium ion is represented by the above formula (1), and it is particularly preferable that the alkylammonium ion is $CH_3N^+H_3$, $C_2H_5N^+H_3$, $(CH_3)_2N^+H_2$, $(C_2H_5)_2N^+H_2$, $(C_4H_9)_2N^+H_2$, $(C_5H_{11})_2N^+H_2$, $(CH_3)_3N^+H$, $(C_2H_5)_3N^+H$, $(C_4H_9)_3N^+H$, $(C_5H_{11})_3N^+H$, $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(C_3H_7)_4N^+$, $(C_4H_9)_4N^+$, $H_3N^+(CH_2)_4N^+H_3$,

20

$\text{H}_2\text{C}=\text{CHCH}_2\text{N}^+\text{HCH}_3$, $\text{H}_3\text{N}^+(\text{CH}_2)_4\text{N}^+\text{H}_2(\text{CH}_2)_4\text{N}^+\text{H}_3$, $\text{HC}\equiv\text{CCH}_2\text{N}^+\text{H}_2$,
 $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{N}^+\text{H}_3$, $\text{H}_3\text{N}^+(\text{CH}_2)_5\text{OH}$, $\text{H}_3\text{N}^+\text{CH}(\text{CH}_2\text{OH})_2$,
 $(\text{HOCH}_2)_2\text{C}(\text{CH}_2\text{N}^+\text{H}_3)_2$, $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{N}^+\text{H}_3$,

5



It is most preferable that the alkylammonium ion is
 $(\text{C}_4\text{H}_9)_3\text{N}^+\text{H}$, $(\text{C}_5\text{H}_{11})_3\text{N}^+\text{H}$, $(\text{C}_3\text{H}_7)_4\text{N}^+$ or $(\text{C}_4\text{H}_9)_4\text{N}^+$.

10

The polymeric actuator of the invention has a
 simple structure and can be easily miniaturized.
 Further, even if voltage is increased, production of
 bubbles caused by electrolysis of water present in the
 resin product can be inhibited. Furthermore, the

15

polymeric actuator shows quick response and can generate
 large displacement.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic sectional view of a preferred embodiment of the polymeric actuator capable of applying the present invention, when no voltage is applied.

5 2A is a schematic sectional view showing a preferred relation between the thickness of an electrode and the thickness of a resin product.

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10 Figs. 2B to 2D are each a schematic perspective view partially containing a section and showing the preferred relation between the thickness of an electrode and the thickness of a resin product in another embodiments capable of applying the present invention.

Fig. 3 is a schematic sectional view showing the polymeric actuator of Fig. 1 when a voltage is applied.

15 Fig. 4 is a schematic view showing an embodiment of use application of the polymeric actuator.

Fig. 5 is a schematic sectional view for illustrating a movement of the actuator in the use application of Fig. 4.

20 Fig. 6 is a schematic view showing another embodiment of the polymeric actuator capable of applying the present invention.

Fig. 7 is a schematic view for illustrating a principle of measuring the degree of displacement in

25 Examples 1 to 21 and Comparative Examples 1 and 2.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is described below in detail with reference to the attached drawings.

- 5 The present invention relates to the improvements of a polymeric actuator comprising an ion-exchange resin product and metal electrodes which are formed on the surface of the ion-exchange resin product and are insulated from each other, said polymeric actuator
10 operating as an actuator by applying a potential difference between the metal electrodes when the ion-exchange resin product is in the water-containing state to allow the ion-exchange resin product to undergo bending or deformation, and a process for producing the
15 same.

First, with reference to Figs. 1 and 2A, a polymeric actuator capable of applying the present invention will be concretely described.

- Fig. 1 is a schematic sectional view of an
20 embodiment of the polymeric actuator capable of applying the present invention. Fig. 2A is a schematic sectional view showing a preferred relation between the thickness of an electrode and the thickness of a resin product.
As shown in Figs. 1 and 2A, the polymeric actuator 1 of
25 the embodiment comprises an ion-exchange resin product 2

in the form of a slender rectangular flat plate (or film) and electrodes 3a, 3b which are formed on the surfaces of the ion-exchange resin product, respectively, and are insulated from each other. This

5 polymeric actuator 1 is so designed that the ion-exchange resin product is bent or deformed by applying a potential difference between the electrodes 3a, 3b when the ion-exchange resin product 2 is in the water-containing state.

10 As shown in Fig. 1, to the electrodes 3a, 3b, one ends of a pair of lead wires 4a, 4b are electrically connected, respectively, and the other ends of the lead wires 4a, 4b are connected to a power source 5.

The form of the ion-exchange resin product 2 is not

15 limited to the rectangular flat plate or film, and the resin product may be in the form of a film, a column or, as shown in Figs. 2B to 2D or Fig. 6, a cylinder.

Examples of the ion-exchange resins for forming the ion-exchange resin product 2 include cation-exchange

20 resins and amphoteric ion-exchange resins. Of these, the cation-exchange resins are preferably employed because they can increase the degree of displacement of the polymeric actuator.

The cation-exchange resins employable herein are,

25 for example, those wherein functional groups such as

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sulfonic acid group and carboxyl group are introduced into polyethylene, polystyrene or fluororesins. In particular, the cation-exchange resins wherein functional groups such as sulfonic acid group and carboxyl group are introduced into fluororesins are preferable.

It is desirable that the cation-exchange resin has an ion-exchange capacity of 0.8 to 3.0 meq/g, preferably 1.4 to 2.0 meq/g. When a cation-exchange resin having such ion-exchange capacity is employed, the degree of displacement of the polymeric actuator can be further increased.

In the present invention, examples of metals for constituting the electrodes 3a, 3b include gold, platinum, palladium, rhodium and ruthenium.

The thickness of the electrodes formed on the surface of the ion-exchange resin product can be optionally determined in accordance with the shapes or materials of the ion-exchange resin product and the electrodes, or positions at which the electrodes are formed.

For example, when the ion-exchange resin product used is in the form of a plate or a film as shown in Fig. 2A, the electrode provided on each surface of the ion-exchange resin product desirably has such a

thickness that the ratio of the thickness a_1 of the metal electrode formed on the ion-exchange resin product to the thickness b_1 of the ion-exchange resin product including the metal electrodes (a_1/b_1) is in the range of 0.03 to 0.40, preferably 0.15 to 0.30. If the a_1/b_1 ratio is in this range, a polymeric actuator capable of generating large displacement and having low surface resistance can be obtained.

In the present invention, when the ion-exchange resin product is in the form of a cylinder (Fig. 2B), the metal electrodes may be provided on the outer surface of the cylinder, the inner surface thereof (Fig. 2C) or both of the outer and the inner surfaces thereof (Fig. 2D). In such cases, the relation between the thicknesses of the ion-exchange resin product and electrode can be also optionally determined.

In case of the polymeric actuator 40 as shown in Fig. 2B in which the metal electrodes 43 are provided on the outer surface of the cylindrical ion-exchange resin product 41, the ratio of the thickness a_2 of the metal electrode 43 to the thickness b_2 of the cylindrical ion-exchange resin product 41 including the metal electrodes 43 (a_2/b_2) is desirably in the range of 0.02 to 0.70, preferably 0.30 to 0.50. If the a_2/b_2 ratio is in this range, a polymeric actuator capable of generating large

displacement and having low surface resistance can be obtained.

In case of the polymeric actuator 50 as shown in Fig. 2C in which the metal electrodes 55 are provided on the inner surface of the cylindrical ion-exchange resin product 51, the ratio of the thickness a_3 of the metal electrode 55 to the thickness b_3 of the cylindrical ion-exchange resin product 51 including the metal electrode 55 (a_3/b_3) is desirably in the range of 0.02 to 0.70, preferably 0.30 to 0.50. If the a_3/b_3 ratio is in this range, a polymeric actuator capable of generating large displacement and having low surface resistance can be obtained.

In case of the polymeric actuator 60 as shown in Fig. 2D in which the metal electrodes 63, 65 are provided on both of the outer and the inner surfaces of the cylindrical ion-exchange resin product 61, respectively, the ratio of the thickness C of the cylindrical ion-exchange resin product 61 excluding the metal electrodes 63, 65 to the thickness b_4 of the cylindrical ion-exchange resin product 61 including the metal electrodes 63, 65 (C/b_4) is desirably in the range of 0.20 to 0.95, preferably 0.45 to 0.70. Further, the ratio of the thickness a_4 of the metal electrode 63 provided on the outer surface of the cylindrical resin

product 61 to the thickness a_5 of the metal electrode 65 provided on the inner surface of the cylindrical resin product 61 (a_4/a_5) is desirably in the range of 0.05 to 20.0, preferably 0.50 to 2.00. If the C/b_4 ratio and
5 the a_4/a_5 ratio are in these ranges, a polymeric actuator capable of generating large displacement and having low surface resistance can be obtained.

In the process for producing the polymeric actuators of the present invention, the electrodes as
10 described above is prepared by the following method.

That is, the process for producing the polymeric actuator of the invention comprises the following steps:

- (i) a step of allowing the ion-exchange resin product to adsorb a metal complex in an aqueous solution
15 (adsorption step),
- (ii) a step of reducing the metal complex adsorbed on the ion-exchange resin product by a reducing agent to deposit a metal on the surface of the ion-exchange resin product (deposition step), and
- 20 (iii) a step of washing the ion-exchange resin product having the deposited metal (washing step).

Examples of the metal complexes employable in the process of the invention include gold complex, platinum complex, palladium complex, rhodium complex and
25 ruthenium complex. Of these, preferable are gold

complex and platinum complex, and particularly preferable is gold complex because the displacement generated by the polymeric actuator can be increased.

- 5 The adsorption of the metal complex on the ion-exchange resin product is carried out by immersing the ion-exchange resin product in an aqueous solution containing the metal complex. Prior to the formation of metal electrode, the ion-exchange resin product may be subjected to any of the following treatments. Each of
- 10 the treatments can be carried out singly or in combination.

(1) Water treatment

The ion-exchange resin product is boiled in hot water.

- 15 (2) Hydrochloric acid treatment

The ion-exchange resin product is held in dilute hydrochloric acid of about 25 vol %.

(3) NaOH treatment

- 20 The ion-exchange resin product is held in a sodium hydroxide aqueous solution of about 0.1N.

(4) Alcohol treatment

The ion-exchange resin product is immersed in an alcohol such as methanol or ethanol.

(5) Autoclave treatment

The ion-exchange resin product is heated at a temperature of 110 to 150 °C in an autoclave.

The reduction of the metal complex is carried out by immersing the ion-exchange resin product adsorbing
5 the metal complex thereon in an aqueous solution containing a reducing agent.

As the reducing agent, sodium sulfite, hydrazine, potassium boron hydride or the like is employable, though the reducing agent used varies depending upon the
10 type of the metal complex used. During the reduction of the metal complex, an acid or an alkali may be added if desired.

The above steps (i) to (iii) may be repeatedly conducted to form the metal electrodes on the surface of
15 the ion-exchange resin product and further inside the resin product.

The number of cycles of the above steps is in the range of preferably 1 to 20, more preferably 4 to 9. The term "number of cycles" means the number of metal
20 complex adsorption-reduction processes conducted on the metal film initially formed by allowing the ion-exchange resin product to adsorb a metal complex and then reducing the metal complex. The number of cycles is preferably utmost 20 because the effect of increasing

the degree of displacement is hardly exerted when the number of cycles is more than 20.

- In the reduction of the metal complex adsorbed on the ion-exchange resin product, the metal complex is
- 5 contacted with the reducing agent to deposit a metal on the surface of the ion-exchange resin product.
- Subsequently, the metal complex present inside the film moves to the vicinity of the film surface (toward the deposited metal) and is then reduced to deposit a metal.
- 10 That is, crystal growth of a metal proceeds from the surface of the ion-exchange resin product to the interior thereof. Therefore, deposition of the metal is conducted not only on the surface of the ion-exchange resin product but also in the interior near the surface.
- 15 As a result, the contact area between the ion-exchange resin product and the metal electrode becomes larger than that in the conventional chemical plating method. Accordingly, by the repetition of the adsorption-deposition process as in the present invention, the
- 20 metal deposition further proceeds inside the ion-exchange resin product, whereby the contact area between the ion-exchange resin product and the metal electrode is furthermore increased. With increase of the contact area, the number of electrode active spots is increased,
- 25 and the number of ions migrating to the electrode is

also increased. Hence, the difference in the water content between the electrodes becomes much larger, and as a result the degree of bending (deformation), namely, degree of displacement, is increased. Moreover, because
5 of the increased contact area between the ion-exchange resin product and the metal electrode, the surface resistance of the electrode is decreased to raise conductivity of the electrode, and the degree of displacement is increased.

- 10 When the metal electrodes are formed by further repeating the above steps (i) to (iii), the degree of displacement of the element can be made much larger than that of the conventional polymeric actuators.

- Then, the ion-exchange resin product having metal
15 electrodes formed by the reduction of a metal complex is preferably subjected to a washing step to remove the unreacted metal complex and reducing agent.

- Examples of the washing liquids preferably used include water, a sodium hydroxide aqueous solution, a
20 sulfuric acid aqueous solution and a hydrochloric acid aqueous solution. When these washing liquids are used, the unreacted metal complex and reducing agent can be efficiently removed. In the use of these washing liquids, it is preferred that the concentration of the
25 sodium hydroxide aqueous solution be in the range of

- 0.01 to 5.0 mol/liter, preferably 0.1 to 1 mol/liter; the concentration of the sulfuric acid aqueous solution be in the range of 0.01 to 6 mol/liter, preferably 0.1 to 6 mol/liter; and the concentration of the hydrochloric acid aqueous solution be in the range of 0.01 to 6 mol/liter, preferably 0.1 to 3 mol/liter.

- Prior to the formation of the metal electrodes through the above steps, the ion-exchange resin product may be subjected to a surface roughening treatment.
- 10 Examples of the surface roughening treatments include a sandblasting treatment and a sandpaper treatment. The surface of the ion-exchange resin product is roughened to such an extent that only a skin layer of the resin product is abraded.
- 15 By virtue of the roughening treatment, the contact area between the surface of the ion-exchange resin product and the electrode formed thereon is increased, and hence the displacement of the polymeric actuator can be increased.
- 20 When the ion-exchange resin product is in the form of a film, insulation of the electrode formed as above can be achieved by cutting edges of the resin product having the electrode thereon. When the ion-exchange resin product is in the form of a cylinder or a column,
- 25 the insulation between the electrodes can be conducted

by irradiating the resin product having the metal electrode thereon with a laser beam to remove a part of the metal electrode and thereby provide insulating zones between the electrodes.

- 5 After the formation of the electrodes on the ion-exchange resin product, the resin product may be subjected to the aforesaid treatments (1) to (5).

- On the thus formed electrodes, an additional electrode layer may be provided. The additional
- 10 electrode layer can be formed by chemical plating, electroplating, vacuum deposition, sputtering, coating, press bonding, welding or the like. Material of the additional electrode layer may be the same as or different from those of the metal electrodes formed on
- 15 the surface and the interior of the ion-exchange resin product. By the provision of the additional electrode layer, the displacement of the polymeric actuator can be further increased.

- Because the polymeric actuator produced by the
- 20 process of the invention as described above can increase the degree of replacement by the above principle, the counter ions of the ion-exchange resin product are not particularly limited, and may be Na^+ or H^+ , or may be alkylammonium ions as used in the polymeric actuator of
- 25 the present invention. However, in the polymeric

actuator, it is particularly preferred that the counter ions contained in the ion-exchange resin product are the alkylammonium ions, for the reason described below.

The polymeric actuator of the present invention
5 comprises an ion-exchange resin product containing as a counter ion, an alkylammonium ion and electrodes which are formed on the surface of the ion-exchange resin product and are insulated from each other.

The polymeric actuator of the invention can be
10 produced by immersing the ion-exchange resin product having, on its surface, metal electrodes insulated from each other in an aqueous solution containing alkylammonium ions to exchange the counter ions with the alkylammonium ions. In the polymeric actuator of the
15 present invention, an aqueous solution of an alkylammonium salt such as chloride bioxide or iodide of the alkylammonium is generally used for exchanging the counter ions.

In the aqueous solution, the alkylammonium salt is
20 contained in an amount equal to or more than that of the functional group of the ion-exchange resin, that is, the concentration of the alkylammonium salt is in the range of 0.01 to 10 mol/l, preferably 0.1 to 1.0 mol/l.

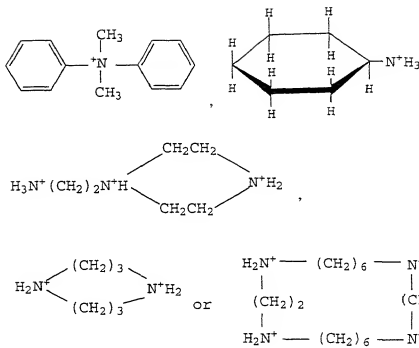
It is preferable that the alkylammonium ions
25 contain alkylammonium ions represented by the following

formula (1). It is also preferable that the alkylammonium ions are alkylammonium ions represented by the following formula (1).



In the above formula, R^1 to R^4 may be the same or different and are each a hydrogen atom, a hydrocarbon group, an oxygen-containing hydrocarbon group or a nitrogen-containing hydrocarbon group, at least one of R^1 to R^4 is a group other than a hydrogen atom, and two or more of R^1 to R^4 may be bonded to form a ring.

As the alkylammonium ions represented by the formula (1), preferable are $CH_3N^+H_3$, $C_2H_5N^+H_3$, $(CH_3)_2N^+H_2$, $(C_2H_5)_2N^+H_2$, $(CH_3)_3N^+H$, $(C_2H_5)_3N^+H$, $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(C_3H_7)_4N^+$, $(C_4H_9)_4N^+$, $H_3N^+(CH_2)_4N^+H_3$, $H_2C=CHCH_2N^+HCH_3$, $H_3N^+(CH_2)_4N^+H_2(CH_2)_4N^+H_3$, $HC\equiv CCH_2N^+H_2$, $CH_3CH(OH)CH_2N^+H_3$, $H_3N^+(CH_2)_5OH$, $H_3N^+CH(CH_2OH)_2$, $(HOCH_2)_2C(CH_2N^+H_3)_2$, $C_2H_5OCH_2CH_2N^+H_3$,



More preferable are $(\text{C}_4\text{H}_9)_3\text{N}^+\text{H}$, $(\text{C}_5\text{H}_{11})_3\text{N}^+\text{H}$, $(\text{C}_3\text{H}_7)_4\text{N}^+$ and $(\text{C}_4\text{H}_9)_4\text{N}^+$. These alkylammonium ions may be used singly

5 or in combination of two or more kinds.

In the polymeric actuator of the present invention, the process for forming the metal electrodes is not limited and, for example, can be formed by any conventional methods.

10 In order that the polymeric actuator of the invention and that prepared by the process of the work, the ion-exchange resin product is required to be in a water-containing state. The expression "water-containing state" used herein means that counter ions

15 can immigrate corresponding to a potential difference

because the ion-exchange resin product contains water.
In the present invention, the polymeric actuator can
work even in water or in the atmosphere of high
humidity, with the proviso that it is in such water-
5 containing state.

Hereinafter, the working principle of the polymeric
actuator will be further described with referring to
Fig. 3.

That is, as shown in Fig. 3, when a potential
10 difference is applied to the surfaces of the ion-
exchange resin product 2 through the metal electrodes
3a, 3b insulated from each other, the positive ions 6
migrate to the cathode side (in Fig. 3, electrode 3a) in
the ion-exchange resin product 2, and the water
15 molecules accompanying the positive ions 6 also migrate
in the resin product 2. As a result, the water content
in the vicinity of the cathode (electrode 3a) is
increased to swell and expand the cathode side of the
resin product 2, while the water content in the vicinity
20 of the anode (opposite side, in Fig. 3, electrode 3b) is
decreased to contract the anode side of the resin
product 2. Thus, by virtue of the difference in the
water content between the electrodes 3a, 3b, the ion-
exchange resin product 2 is bent.

In the polymeric actuator of the invention, since the water molecules migrate together with the ions, and the ions having large ionic radius such as alkylammonium ions are used as the migrating ions, the difference in the water content between the electrodes is further increased, and, as a result, the degree of bending (deformation), namely, degree of displacement, is increased. That is, the polymeric actuator of the invention generates larger displacement of element as compared with the conventional polymeric actuators. In the polymeric actuator of the invention containing alkylammonium ions, further, water contained in the ion-exchange resin product is hardly electrolyzed even if a high voltage is applied, and therefore production of bubbles can be inhibited, differently from the conventional polymeric actuators wherein Na^+ or H^+ ions are contained. Hence, a higher voltage than that applied to the conventional polymeric actuators can be applied to the polymeric actuator of the invention, and hence the response of the polymeric actuator can be improved.

When a direct-current voltage of 0.1 to 3 V is applied between the electrodes of the polymeric actuator prepared by a process of the present invention, the polymeric actuator can obtain a displacement of about

0.5 to 3 times as large as the element within several seconds. While, when a direct-current voltage of 0.1 to 4 V is applied between the electrodes of the polymeric actuator of the invention, the polymeric actuator can
5 obtain a displacement of about 1 to 3 times the length of the element within several seconds. Further, the polymeric actuator can undergo flexible movement in water.

An embodiment of use application of the polymeric
10 actuators as described above is a guide shown in Figs. 4 and 5.

In this application, a guide wire 11 as the guide consists of a linear member 12 made of, for example, a slender synthetic resin tube or a slender stainless tube
15 and a polymeric actuator 13 joined to a tip of the linear member 12.

The actuator 13 comprises an ion-exchange resin product 14 in the form of a slender rectangular flat plate and a pair of electrodes 15a, 15b disposed on both
20 surfaces of the resin product, which can be formed by the method of the invention. By applying a voltage between the electrodes 15a, 15b, the polymeric actuator 13 is bent in two directions.

To the electrodes 15a, 15b, one ends of a pair of
25 lead wires 16a, 16b are electrically connected,

respectively. The lead wires 16a, 16b extend inside the linear member 12, and the other ends of the lead wires 16a, 16b are connected to an operation controller 17.

The operation controller 17 is equipped with a
5 switchable operating lever 18. By operating the lever 18, the direction of the current from a power source 20 to the lead wires 16a, 16b can be switched by way of a double-pole double-throw switch 19 incorporated inside the operation controller 17.

10 Referring to Fig. 5, when the double-pole double-throw switch 19 is positioned as indicated by the solid line, one lead wire 16a is connected to a positive electrode 15a and the other lead wire 16b is connected to a negative electrode 15b, whereby the actuator 13
15 bent as indicated by the broken lines in Fig. 5. If the double-pole double-throw switch 19 is switched by the operating lever 18 of the operation controller 17 through a neutral position to the position indicated by the broken line in Fig. 5, the lead wire 16a is
20 connected to a negative electrode 15b and the lead wire 16b is connected to a positive electrode 15a, whereby the actuator 13 is reversely bent to the position indicated by the two-dot chain line in Fig. 5.

Thus, the polymeric actuator 13 can be arbitrarily and positively deformed by the switching operation between the anode and the cathode.

- Another embodiment of use application of the
5 polymeric actuator as described above is a cylindrical polymeric actuator 40 shown in Fig. 6.

- In the production of the cylindrical polymeric actuator according to the process of the invention, metal electrodes are formed in the following manner.
10 First, a metal complex is adsorbed on an ion-exchange resin product 41 and reduced by a reducing agent in accordance with the aforesaid method to deposit a metal on the surface of the ion-exchange resin product 41. The metal complex adsorption-reduction operation and the
15 metal deposition operation are repeated to grow the deposited metal, whereby a metal layer extending from the surface of the ion-exchange resin product 41 to the interior thereof is formed.

- Then, the cylindrical ion-exchange resin product 41
20 provided with a metal layer on the outer surface is irradiated with a laser beam from a laser beam machine to remove the irradiated metal layer, whereby insulating zones 42 in the form of groove and metal electrodes 43a, 43b, 43c, 43d which are electrically insulated from each
25 other by the zones 42 are formed.

In the polymeric actuator shown in Fig. 6, to the metal electrodes 43a, 43b, 43c and 43d, one ends of lead wires 44a, 44b, 44c and 44d are electrically connected, respectively. This polymeric actuator can be bent in four directions by applying a voltage between the electrodes 43a and 43c oppositely positioned across the ion-exchange resin product 41 and between the electrodes 43b and 43d oppositely positioned across the ion-exchange resin product 41. The polymeric actuator can also undergo rotating by combining the bending directions.

Such metal electrodes as mentioned above may be provided on the inner surface of the ion-exchange resin product, or may be provided on both of the inner and the outer surfaces of the resin product.

EFFECT OF THE INVENTION

According to the process for preparing polymeric actuator of the invention, since a metal electrode is formed by repeating the specific steps as described above, the contact area between the ion-exchange resin product and the metal electrode can be increased to make the quantity of ions migrating to the electrode increased, and the thickness of the metal electrodes can be increased to reduce the surface resistance of the

electrodes, thereby to improve the conductivity thereof. Therefore, the polymeric actuator thus obtained is high in the degree of bending (deformation), namely, degree of displacement and exhibits quick response.

- 5 According to the process of the invention, therefore, a polymeric actuator having simple structure, capable of being miniaturized, showing quick response, generating large displacement and capable of working with low power can be obtained.
- 10 In the polymeric actuator of the invention, since the counter ion of the ion-exchange resin product is exchanged with a specific alkylammonium ion, the quantity of water molecules which migrate together with the alkylammonium ions by the application of the
- 15 potential difference is increased, whereby the difference in the water content between the electrodes becomes much larger, and even if a high voltage is applied between the electrodes of the polymeric actuator, electrolysis of water in the ion-exchange
- 20 resin product hardly takes place and production of bubbles is inhibited, differently from the generally used ion-exchange resins whose counter ion is Na^+ or H^+ . Accordingly, in the polymeric actuator of the invention, the degree of bending (deformation), namely, degree of
- 25 displacement, is increased, and a higher voltage than

that applied to the conventional polymeric actuators can be applied to the polymeric actuator of the invention, and hence the response can be quickened.

According to the invention, therefore, a polymeric
5 actuator having simple structure, capable of being easily miniaturized, showing quick response, generating large displacement, capable of working with low power and free from occurrence of bubbles due to electrolysis of water even when a potential difference is increased
10 in order to increase the displacement can be obtained.

If the polymeric actuator of the invention or the polymeric actuator obtained by the process of the invention is used as a guide means for surgical equipment for microsurgery, such as scissors, forceps,
15 snare, laser knife and spatula, or microdevices such as various sensors and tools, the guidance can be improved because the polymeric actuator can be arbitrarily and positively bent (deformed) by the operation of the operation controller. As a result, the surgical
20 equipment or the microdevices can be turned toward the desired place, and the turning operation can be rapidly and easily performed without skill.

If the polymeric actuator of the invention or the polymeric actuator of the invention is applied to
25 surgical equipment such as tweezers, scissors, forceps,

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snare, laser knife, spatula and clip used for the microsurgery such as eye-ball operation, intra-cavity endoscopic operation and microvein suture operation, pain inflicted on the patients in the tests or

- 5 treatments can be greatly eased, and physical or mental burden on the patients can be reduced.

- If the polymeric actuators are applied to various sensors or repair tools to inspect or repair facilities of plants such as power plant, and mechanical systems
10 such as air craft engines or the like (particularly for piping system or engine interior), the inspection or the repairing can be surely performed without much labor or time.

- In addition to the above application, the polymeric
15 actuator of the invention or the polymeric actuator obtained by the process of the invention can be favorably applied to high-frequency vibrating micropumps, health machines such as auxiliary power massage machine for rehabilitation, hygrometers,
20 hygrometer controlling devices, soft manipulators, submerged valves, industrial machinery such as soft conveyor, underwater mobiles such as artificial goldfish and artificial seaweed, and hobby goods such as moving fishing bait and propulsive fin.

EXAMPLE

The present invention is further described with reference to the following examples, but it should be construed that the invention is in no way limited to those examples.

In Examples and Comparative Examples, the measurement of the degree of displacement was carried out as follows: as shown in Fig. 7, at the position of 8 mm from one end of the specimen 101, the specimen was interposed between platinum plates, and the specimen 101 with the platinum plates was held in water. Lead wires 103a, 103b were extended from the platinum plates and connected to a potentiostat 105. A voltage was applied between the gold electrodes 107a, 107b on the both sides of the specimen 101. The degree of displacement was determined by measuring a displacement at the position of 10 mm from the fixed end by means of a laser displacement meter.

20 Example 1

A filmy fluororesin type ion-exchange resin product having a film thickness of 140 μm (ion-exchange capacity: 1.4 meq/g) was subjected to a surface roughening treatment with alumina particles of #800. Then, the ion-exchange resin product was subjected to

two cycles of the following steps (1) to (3) to form gold electrodes on the surfaces of the resin product.

(1) Adsorption step

The ion-exchange resin product is immersed in an aqueous solution of phenanthrine gold chloride for 24 hours to allow the resin product to adsorb a phenanthrine gold complex.

(2) Deposition step

In an aqueous solution containing sodium sulfite and NaOH, the adsorbed phenanthrine gold complex is reduced to form gold electrodes on the surfaces of the ion-exchange resin product. The reduction of the phenanthrine gold complex is carried out at an aqueous solution temperature of 60 to 80 °C for 6 hours with slowly adding sodium sulfite.

(3) Washing step

The ion-exchange resin product on the surfaces of which gold electrodes have been formed is taken out and washed with water at 70 °C for 1 hour.

The resulting ion-exchange resin product provided with gold electrodes was cut to give a specimen having a size of 1.0 mm × 20 mm, and the surface resistance of the specimen was measured. Then, a voltage (square wave of 0.1 Hz and 2.0 V) was applied to the specimen through

the electrodes on the front and back sides to measure the degree of displacement (bending).

The degree of displacement of the specimen was 2.0 mm, and the surface resistance of the specimen was 10 Ω .

5

Example 2

A specimen was prepared in the same manner as in Examples 1, except that the steps (1) to (3) were repeated 3 cycles. The specimen was evaluated in the same manner as in Example 13.

10

As a result, the degree of displacement of the specimen was 3.2 mm, and the surface resistance of the specimen was 5 Ω .

15 Example 3

A specimen was prepared in the same manner as in Examples 1, except that the steps (1) to (3) were repeated 4 cycles. The specimen was evaluated in the same manner as in Example 13.

20

As a result, the degree of displacement of the specimen was 3.7 mm, and the surface resistance of the specimen was 2 Ω .

Example 4

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A specimen was prepared in the same manner as in Examples 1, except that the steps (1) to (3) were repeated 5 cycles. The specimen was evaluated in the same manner as in Example 13.

- 5 As a result, the degree of displacement of the specimen was 3.9 mm, and the surface resistance of the specimen was 1 Ω .

Example 5

- 10 A specimen was prepared in the same manner as in Examples 1, except that the steps (1) to (3) were repeated 6 cycles. The specimen was evaluated in the same manner as in Example 13.

- 15 As a result, the degree of displacement of the specimen was 4.2 mm, and the surface resistance of the specimen was 1 Ω .

Example 6

- 20 A specimen was prepared in the same manner as in Examples 1, except that the steps (1) to (3) were repeated 7 cycles. The specimen was evaluated in the same manner as in Example 13.

- 25 As a result, the degree of displacement of the specimen was 4.5 mm, and the surface resistance of the specimen was 0.5 Ω .

Example 7

A specimen was prepared in the same manner as in Examples 1, except that the steps (1) to (3) were repeated 8 cycles. The specimen was evaluated in the same manner as in Example 13.

As a result, the degree of displacement of the specimen was 5.0 mm, and the surface resistance of the specimen was 0.5 Ω .

10

Example 8

A specimen was prepared in the same manner as in Examples 1, except that the steps (1) to (3) were repeated 9 cycles. The specimen was evaluated in the same manner as in Example 13.

15

As a result, the degree of displacement of the specimen was 5.3 mm, and the surface resistance of the specimen was 0.5 Ω .

20 Example 9

A specimen was prepared in the same manner as in Examples 1, except that the steps (1) to (3) were repeated 10 cycles. The specimen was evaluated in the same manner as in Example 13.

As a result, the degree of displacement of the specimen was 5.5 mm, and the surface resistance of the specimen was 0.5 Ω .

5 Comparative Example 1

A specimen was prepared in the same manner as in Examples 1, except the steps (1) to (3) were not repeated. The specimen was evaluated in the same manner as in Example 13.

- 10 As a result, the degree of displacement of the specimen was 2.0 mm, and the surface resistance of the specimen was 10 Ω .

It can be seen from the above results that, as the number of cycles of the steps (1) to (3) becomes larger, a polymeric actuator exhibiting larger displacement and lower surface resistance can be obtained. It can be also seen that the effect on the degree of displacement and the surface resistance becomes greater especially when the number of cycles is 4 to 9.

20

Example 10

A rectangular ion-exchange resin product provided with gold electrodes (ion-exchange capacity: 1.8 meq/g) was cut into a size of 1.0 mm x 20 mm and immersed in a

- 25 0.5M (C₂H₅)₃NH₃Cl aqueous solution for 24 hours to give a

specimen. Then, a voltage (square wave of 0.1 Hz and 1.5 V) was applied to the specimen through the electrodes on the front and back sides to measure the degree of displacement. Further, a voltage (square wave of 0.1 Hz) at which bubbles were produced was measured.

The results are set forth in Table 1.

Example 11

A rectangular ion-exchange resin product provided with gold electrodes (ion-exchange capacity: 1.8 meq/g) was cut into a size of 1.0 mm × 20 mm and immersed in a 0.5M (CH₃)₂NH₂Cl aqueous solution for 24 hours to give a specimen. Then, a voltage (square wave of 0.1 Hz and 1.5 V) was applied to the specimen through the electrodes on the front and back sides to measure the degree of displacement. Further, a voltage (square wave of 0.1 Hz) at which bubbles were produced was measured.

The results are set forth in Table 1.

Example 12

A rectangular ion-exchange resin product provided with gold electrodes (ion-exchange capacity: 1.8 meq/g) was cut into a size of 1.0 mm × 20 mm and immersed in a 0.5M (C₂H₅)₃NHCl aqueous solution for 24 hours to give a specimen. Then, a voltage (square wave of 0.1 Hz and

1.5 V) was applied to the specimen through the electrodes on the front and back sides to measure the degree of displacement. Further, a voltage (square wave of 0.1 Hz) at which bubbles were produced was measured.

5 The results are set forth in Table 1.

Example 13

000120.0005260
A rectangular ion-exchange resin product provided with gold electrodes (ion-exchange capacity: 1.8 meq/g)
10 was cut into a size of 1.0 mm × 20 mm and immersed in a 0.5M (C₃H₇)₄NCl aqueous solution for 24 hours to give a specimen. Then, a voltage (square wave of 0.1 Hz and 1.5 V) was applied to the specimen through the electrodes on the front and back sides to measure the
15 degree of displacement. Further, a voltage (square wave of 0.1 Hz) at which bubbles were produced was measured.

 The results are set forth in Table 1.

Example 14

20 A rectangular ion-exchange resin product provided with gold electrodes (ion-exchange capacity: 1.8 meq/g) was cut into a size of 1.0 mm × 20 mm and immersed in a 0.5M (C₄H₉)₄NCl aqueous solution for 24 hours to give a specimen. Then, a voltage (square wave of 0.1 Hz and
25 1.5 V) was applied to the specimen through the

electrodes on the front and back sides to measure the degree of displacement. Further, a voltage (square wave of 0.1 Hz) at which bubbles were produced was measured.

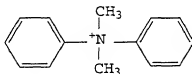
The results are set forth in Table 1.

5

Example 15

A rectangular ion-exchange resin product provided with gold electrodes (ion-exchange capacity: 1.8 meq/g) was cut into a size of 1.0 mm x 20 mm and immersed in an aqueous solution (concentration: 0.5 M) of a chloride of an alkylammonium ion represented by the following formula for 24 hours to give a specimen. Then, a voltage (square wave of 0.1 Hz and 1.5 V) was applied to the specimen through the electrodes on the front and back sides to measure the degree of displacement. Further, a voltage (square wave of 0.1 Hz) at which bubbles were produced was measured.

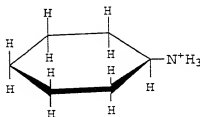
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The results are set forth in Table 1.

Example 16

- A rectangular ion-exchange resin product provided with gold electrodes (ion-exchange capacity: 1.8 meq/g) was cut into a size of 1.0 mm \times 20 mm and immersed in an aqueous solution (concentration: 0.5 M) of a chloride of an alkylammonium ion represented by the following formula for 24 hours to give a specimen. Then, a voltage (square wave of 0.1 Hz and 1.5 V) was applied to the specimen through the electrodes on the front and back sides to measure the degree of displacement.
- Further, a voltage (square wave of 0.1 Hz) at which bubbles were produced was measured.



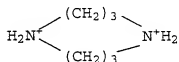
- The results are set forth in Table 1.

Example 17

- A rectangular ion-exchange resin product provided with gold electrodes (ion-exchange capacity: 1.8 meq/g) was cut into a size of 1.0 mm \times 20 mm and immersed in an aqueous solution (concentration: 0.5 M) of a chloride of an alkylammonium ion represented by the following formula for 24 hours to give a specimen. Then, a

voltage (square wave of 0.1 Hz and 1.5 V) was applied to the specimen through the electrodes on the front and back sides to measure the degree of displacement.

- Further, a voltage (square wave of 0.1 Hz) at which
5 bubbles were produced was measured.



The results are set forth in Table 1.

10 Example 18

A rectangular ion-exchange resin product provided with gold electrodes (ion-exchange capacity: 1.8 meq/g) was cut into a size of 1.0 mm × 20 mm and immersed in an aqueous solution (concentration: 0.5 M) of a chloride of

- 15 $\text{H}_2\text{C}=\text{CHCH}_2\text{N}^+\text{H}_2\text{CH}_3$ for 24 hours to give a specimen. Then, a voltage (square wave of 0.1 Hz and 1.5 V) was applied to the specimen through the electrodes on the front and back sides to measure the degree of displacement.

Further, a voltage (square wave of 0.1 Hz) at which

- 20 bubbles were produced was measured.

The results are set forth in Table 1.

Example 19

- A rectangular ion-exchange resin product provided with gold electrodes (ion-exchange capacity: 1.8 meq/g) was cut into a size of 1.0 mm × 20 mm and immersed in an aqueous solution (concentration: 0.5 M) of a chloride of
- 5 $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{N}^+\text{H}_3$ for 24 hours to give a specimen. Then, a voltage (square wave of 0.1 Hz and 1.5 V) was applied to the specimen through the electrodes on the front and back sides to measure the degree of displacement. Further, a voltage (square wave of 0.1 Hz) at which
- 10 bubbles were produced was measured.

The results are set forth in Table 1.

Example 20

- A rectangular ion-exchange resin product provided
- 15 with gold electrodes (ion-exchange capacity: 1.8 meq/g) was cut into a size of 1.0 mm × 20 mm and immersed in an aqueous solution (concentration: 0.5 M) of a chloride of $\text{H}_3\text{N}^+\text{CH}(\text{CH}_2\text{OH})_2$ for 24 hours to give a specimen. Then, a voltage (square wave of 0.1 Hz and 1.5 V) was applied to
- 20 the specimen through the electrodes on the front and back sides to measure the degree of displacement. Further, a voltage (square wave of 0.1 Hz) at which bubbles were produced was measured.

The results are set forth in Table 1.

Example 21

- A rectangular ion-exchange resin product provided with gold electrodes (ion-exchange capacity: 1.8 meq/g) was cut into a size of 1.0 mm x 20 mm and immersed in an aqueous solution (concentration: 0.5 M) of a chloride of $C_2H_5OCH_2CH_2N^+H_3$ for 24 hours to give a specimen. Then, a voltage (square wave of 0.1 Hz and 1.5 V) was applied to the specimen through the electrodes on the front and back sides to measure the degree of displacement.
- Further, a voltage (square wave of 0.1 Hz) at which bubbles were produced was measured.

The results are set forth in Table 1.

Comparative Example 2

- A rectangular ion-exchange resin product provided with gold electrodes (ion-exchange capacity: 1.8 meq/g) was cut into a size of 1.0 mm x 20 mm and immersed in a 0.1N NaOH aqueous solution for 24 hours to give a specimen. Then, a voltage (square wave of 0.1 Hz and 1.5 V) was applied to the specimen through the electrodes on the front and back sides to measure the degree of displacement. Further, a voltage (square wave of 0.1 Hz) at which bubbles were produced was measured.

The results are set forth in Table 1.

Table 1

	Degree of displacement (mm)	Bubble production voltage (V)
Ex. 10	1.0	2.0
Ex. 11	2.0	2.0
Ex. 12	2.3	2.1
Ex. 13	3.0	2.5
Ex. 14	2.2	4.4
Ex. 15	2.0	4.0
Ex. 16	2.3	2.5
Ex. 17	2.2	2.0
Ex. 18	2.1	2.2
Ex. 19	2.3	2.3
Ex. 20	2.0	1.8
Ex. 21	2.3	2.0
Comp. Ex. 2	0.5	1.8

It can be seen from the above results that the

5 polymeric actuators wherein the counter ions of the ion-exchange resin were exchanged with the alkylammonium ions represented by the formula (1) exhibit larger displacement and higher voltage for bubble production than those of the conventional polymeric actuator of

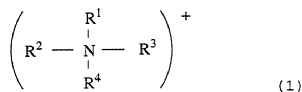
10 Comp. Ex. 1 whose counter ion is Na^+ .

What is claimed is:

1. A process for producing a polymeric actuator comprising an ion-exchange resin product and metal electrodes which are formed on the surface of the ion-exchange resin product and are insulated from each other, said actuator operating as an actuator by applying a potential difference between the metal electrodes when the ion-exchange resin product is in the water-containing state to allow the ion-exchange resin product to undergo bending or deformation,
 - wherein the following steps (i) to (iii) are repeatedly conducted to form the metal electrodes ranging from the surface of the ion-exchange resin product to the inside thereof;
 - (i) a step of allowing the ion-exchange resin product to adsorb a metal complex in an aqueous solution (adsorption step),
 - (ii) a step of reducing the metal complex adsorbed on the ion-exchange resin product by a reducing agent to deposit a metal on the surface of the ion-exchange resin product (deposition step), and
 - (iii) a step of washing the ion-exchange resin product having the deposited metal (washing step).

2. A polymeric actuator comprising an ion-exchange resin product containing an alkylammonium ion as a counter ion and metal electrodes which are formed on the surface of the ion-exchange resin product and are insulated from each other, said polymeric actuator operating as an actuator by applying a potential difference between the metal electrodes when the ion-exchange resin product is in the water-containing state to allow the ion-exchange resin product to undergo bending or deformation.

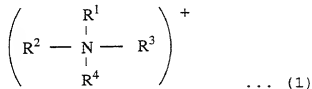
3. The polymeric actuator as claimed in claim 2, wherein the alkylammonium ions are alkylammonium ions containing at least ions represented by the following formula (1):



wherein R^1 to R^4 may be the same or different and are each a hydrogen atom, a hydrocarbon group, an oxygen-containing hydrocarbon group or a nitrogen-containing hydrocarbon group, at least one of R^1 to R^4 is a group other than a hydrogen atom, and two or more of R^1 to R^4 may be bonded to form a ring.

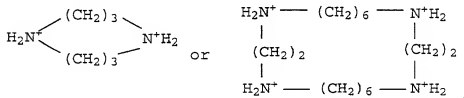
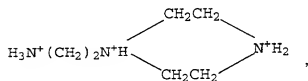
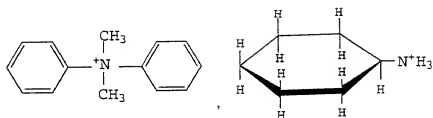
4. The polymeric actuator as claimed in claim 2, wherein the alkylammonium ion is represented by the following formula (1):

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wherein R^1 to R^4 may be the same or different and are each a hydrogen atom, a hydrocarbon group, an oxygen-containing hydrocarbon group or a nitrogen-containing hydrocarbon group, at least one of R^1 to R^4 is a group other than a hydrogen atom, and two or more of R^1 to R^4 may be bonded to form a ring.

5. The polymeric actuator as claimed in any one of claims 2 to 4, wherein the ion represented by the formula (1) is $CH_3N^+H_3$, $C_2H_5N^+H_3$, $(CH_3)_2N^+H_2$, $(C_2H_5)_2N^+H_2$, $(C_4H_9)_2N^+H_2$, $(C_5H_{11})_2N^+H_2$, $(CH_3)_3N^+H$, $(C_2H_5)_3N^+H$, $(C_4H_9)_3N^+H$, $(C_5H_{11})_3N^+H$, $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, $(C_3H_7)_4N^+$, $(C_4H_9)_4N^+$, $H_3N^+(CH_2)_4N^+H_3$, $H_2C=CHCH_2N^+HCH_3$, $H_3N^+(CH_2)_4N^+H_2(CH_2)_4N^+H_3$, $HC\equiv CCH_2N^+H_2$, $CH_3CH(OH)CH_2N^+H_3$, $H_3N^+(CH_2)_5OH$, $H_3N^+CH(CH_2OH)_2$, $(HOCH_2)_2C(CH_2N^+H_3)_2$, $C_2H_5OCH_2CH_2N^+H_3$,



ABSTRACT

The process for producing a polymeric actuator according to the invention is a process for producing a polymeric actuator comprising an ion-exchange resin product and metal electrodes which are formed on the surface of the ion-exchange resin product and are insulated from each other and functioning as an actuator by applying a potential difference between the metal electrodes in such a state that the ion-exchange resin product contains water to allow the ion-exchange resin product to undergo bending or deformation, wherein the following steps (i) to (iii) are repeatedly conducted to form the metal electrodes ranging from the surface of the ion-exchange resin product to the inside thereof;

10 (i) a step of allowing the ion-exchange resin product to adsorb a metal complex (adsorption step), (ii) a step of reducing the metal complex adsorbed on the ion-exchange resin product by a reducing agent to deposit a metal on the surface of the ion-exchange resin product

15 (deposition step), and (iii) a step of washing the ion-exchange resin product having the deposited metal (washing step). By the formation of metal electrodes through the above steps, a polymeric actuator having simple structure, capable of being easily miniaturized,

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showing quick response and capable of generating large displacement can be obtained.

- The polymeric actuator 1 of the invention comprises an ion-exchange resin product 2 in the form of a slender rectangular flat sheet and metal electrodes 3a, 3b which are formed on the surface of the ion-exchange resin product 2 and are insulated from each other, and the polymeric actuator is designed so that the ion-exchange resin product 2 undergoes bending or deformation by applying a potential difference between the metal electrodes in such a state that the ion-exchange resin product contains an alkylammonium ion-containing aqueous solution. This polymeric actuator has excellent flexibility, is lightweight, has quick response and is capable of generating large displacement.

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Fig. 1

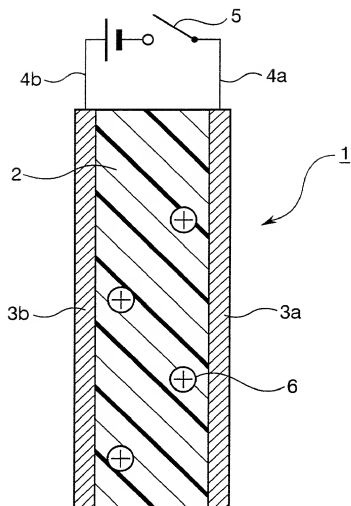


Fig. 2A

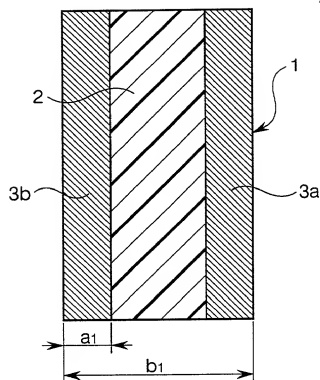


Fig. 2B

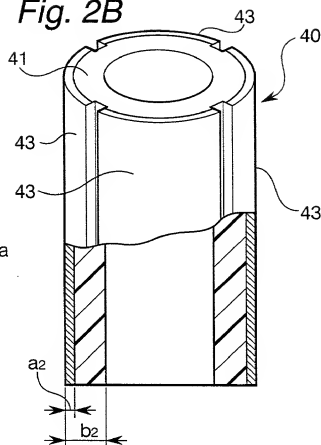


Fig. 2C

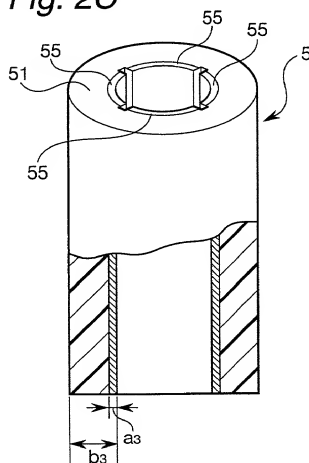


Fig. 2D

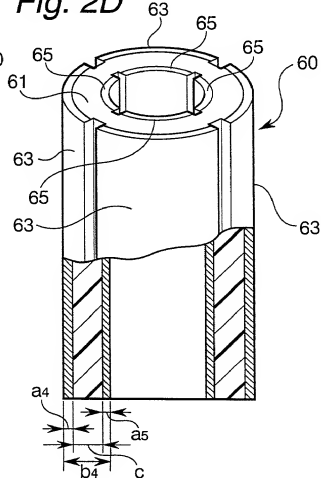


Fig. 3

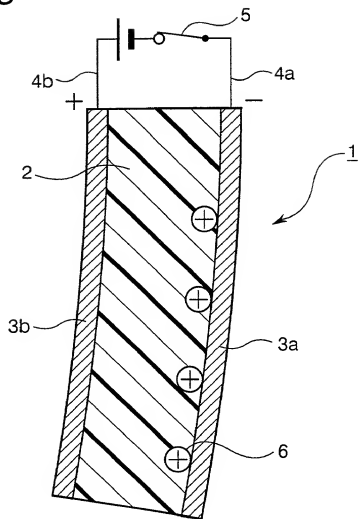


Fig. 4

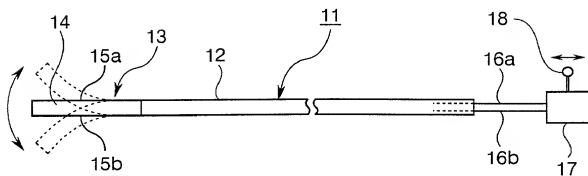


Fig. 5

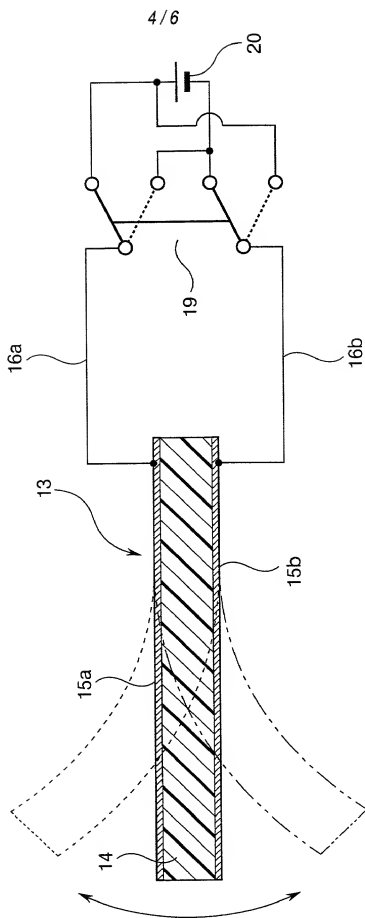


Fig. 6

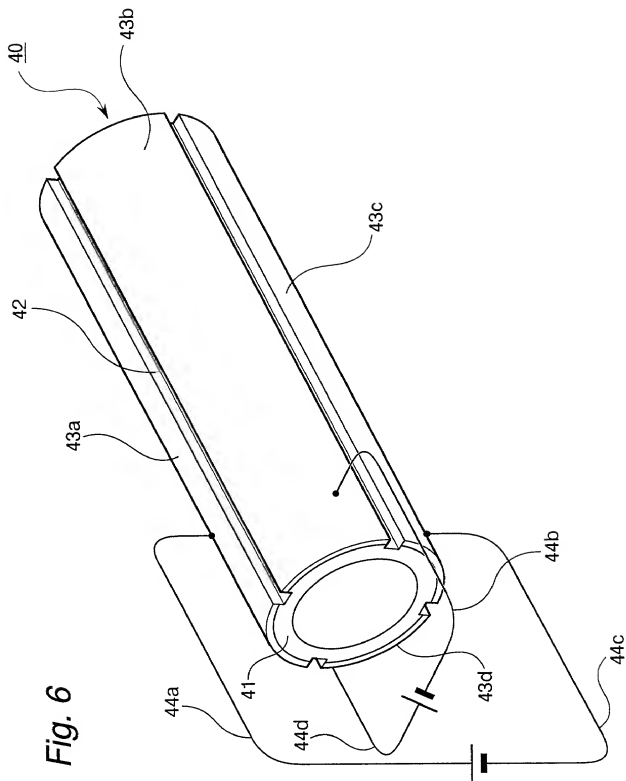
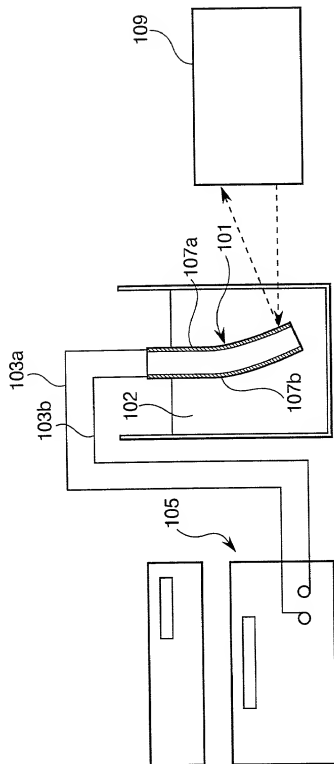


Fig. 7



Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

POLYMERIC ACTUATORS AND PROCESS FOR PRODUCING THE SAME
the specification of which

(check one)

- ☒ is attached hereto.
- ☐ was filed on _____ as
Application Serial No. _____
and was amended on _____
(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
<u>39121/1998</u>	<u>Japan</u>	<u>20/Feb./1998</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
<u>84495/1998</u>	<u>Japan</u>	<u>30/March/1998</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
<u> </u>	<u> </u>	<u> </u>	<input type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration number)

William H. Logsdon	22,132	Barbara E. Johnson	31,198	Lester N. Fortney	38,141
Russell D. Orkin	25,363	Paul M. Reznick	33,059	Randall A. Notzen	36,882
David C. Hanson	23,024	John W. McIlvaine	34,219	Jesse A. Hirshman	40,016
Frederick B. Ziesenheim	19,438	Michael I. Shamos	30,424	James G. Porcelli	33,757
Richard L. Byrne	28,498	Blynn L. Shideler	35,034	Kent E. Baldauf, Jr.	36,082
Kent E. Baldauf	25,826	Julie W. Meder	36,216		

Send Correspondence to:

Russell D. Orkin, 700 Koppers Building, 436 Seventh Avenue, Pittsburgh PA 15219-1818

Direct Telephone calls to: (name and telephone number) Russell D. Orkin (412) 471-8815

Full name of sole or first inventor	Keisuke OGURO
Inventor's signature	<i>Keisuke Oguro</i> Date Feb. 10, 1999
Residence	Ikeda-shi, Osaka, Japan
Citizenship	Japanese
Post Office Address	c/o Osaka National Research Institute, Agency of Industrial Science and Technology, Ministry of International Trade and Industry, 8-31, Midorigaoka 1-chome, Ikeda-shi, Osaka 563-8577, Japan
Full name of second joint inventor, if any	Kinji ASAKA
Second inventor's signature	<i>Kinji Asaka</i> Date Feb. 10, 1999
Residence	Ikeda-shi, Osaka, Japan
Citizenship	Japanese
Post Office Address	c/o Osaka National Research Institute, Agency of Industrial Science and Technology, Ministry of International Trade and Industry, 8-31, Midorigaoka 1-chome, Ikeda-shi, Osaka 563-8577, Japan

(Supply similar information and signature for third and subsequent joint inventors.)

00252633-021099

Full name of third joint inventor, if any

Tatsuhiro OKADA

Third inventor's signature

*T. Okada*Date
Feb. 10, 1999

Residence

Tsukuba-shi, Ibaraki, Japan

Citizenship

Japanese

Post Office Address

c/o National Institute of Materials and Chemical Research,
Agency of Industrial Science and Technology,
Ministry of International Trade and Industry,
1-1, Higashi, Tsukuba-shi, Ibaraki 305-8565, Japan

Full name of fourth joint inventor, if any

Kazuo ONISHI

Fourth inventor's signature

*Kazuo Onishi*Date
Feb. 10, 1999

Residence

Amagasaki-shi, Hyogo, Japan

Citizenship

Japanese

Post Office Address

26-10-304, Mukonosou-Higashi 1-chome,
Amagasaki-shi, Hyogo 661-0032, Japan

Full name of fifth joint inventor, if any

Shingo SEWA

Fifth inventor's signature

*Shingo Sawa*Date
Feb. 10, 1999

Residence

Nakaimachi, Ashigarakami-gun, Kanagawa, Japan

Citizenship

Japanese

Post Office Address

2806-4, Inokuchi, Nakaimachi, Ashigarakami-gun,
Kanagawa 259-0151, Japan

Full name of sixth joint inventor, if any

Sixth inventor's signature

Date

Residence

Citizenship

Post Office Address

00253638-021999